

Modeling Monochloramine Loss and Disinfection By-product Formation in Drinking Water

Project Scope

Monochloramine is the major chloramine produced in a commonly used drinking water disinfection process. Monochloramine, although a weaker disinfectant than chlorine, can be used when free chlorine residuals are difficult to maintain, or when they lead to excessive disinfection by-product (DBP) formation. The fate of chloramines in drinking water distribution systems and the nature of the reactions and byproducts, as well as factors that influence these, are not well-characterized. Several common reactive water contaminants, such as natural organic matter (NOM), play an important role in determining disinfectant stability and the DBP formation. In addition to reacting with organic materials, monochloramine is known to slowly decompose via autooxidation. The kinetics of autodecomposition and other reactions involving monochloramines are also affected by the levels of nitrite, bromide, and NOM, as well as by pH, temperature, ionic strength, and buffering capacity.

The objectives of the research project were to more fully characterize the influence of the nitrite and bromide on: (1) the fate of monochloramine and the nature of inorganic reaction products; (2) the kinetics of monochloramine loss; and (3) the formation of the DBPs, haloacetic acid (HAA), and N-nitrosodimethylamine (NDMA). The researchers also modified and extended existing chloramine reaction models to include the effects of nitrite and bromide. The studies examined the reactivity of NOM from eight different sources, including purified fractionated commercial samples (humic acid) and water from a range of natural sources and treatment facilities. Reaction rates and processes were compared to predictions from kinetic models, and the experimental results were used to adjust and refine the model and parameter values.

Project Results and Implications

Modeling and Measurement of Reactions of Monochloramine with NOM: The investigators modeled monochloramine decay in the presence of NOM as occurring via two distinct pathways; auto-decomposition and direct reaction with NOM. Monochloramine auto-decomposition is complicated but has been well characterized. Sixteen reactions from the literature were incorporated into the decay model.

Grant Title and Principal Investigator

Mechanisms and Kinetics of Chloramine Loss and By-product Formation in the Presence of Reactive Drinking Water Distribution System Constituents (EPA Grant #R826832)

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Key Findings and Implications

Analytical Accomplishments:

- Developed a mixed mechanistic and empirical kinetic model that could accurately predict the rate of monochloramine loss in the presence of natural organic matter (NOM) under a variety of conditions (pH, temperature, ionic strength, buffer intensity) and in the presence of nitrite or bromide.
- The formation of haloacetic acids (HAAs) in the presence or absence of bromide and the formation of N-nitrosodimethylamine (NDMA) was also predicted adequately by the model.

Implications of Research:

- Refined existing models for monochloramine reactions that can be used to more accurately predict levels of disinfectant residuals and DBP formation over a wide range of source water characteristics and treatment parameters.
- Confirmed NDMA formation by a direct reaction between monochloramine and dimethylamine, indicating that NDMA can be a disinfection by-product.

Publications include 5 peer reviewed articles and 7 conference presentations.

Project Period: September 1998 to September 2001

Relevance to ORD's *Drinking Water Research Multi-Year Plan (2003 Edition)*

This project contributes directly to the third of three Long-term Goals for drinking water research: (1) by 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/DPB, and Six-Year Review Rules.

This grant refined a model that adequately predicted monochloramine decay in the presence of natural organic matter and nitrite or bromide for a variety of pH, temperature, ionic strength, and buffering conditions. The model also adequately predicted the formation of haloacetic acid disinfection by-products as well as N-nitrosodimethylamine (NDMA). The investigators concluded that NDMA should be considered a disinfection by-product.

A semi-mechanistic model portraying both the mechanistic autodecomposition pathway and the empirical NOM pathway was developed and revised based on experimental results. Revisions to the monochloramine/NOM reaction model included:

1. The mechanistic model for loss of monochloramine by autodecomposition was adapted to account for loss under a variety of water quality conditions such as pH, temperature, ionic strength, and buffer intensity (carbonate).
2. Monochloramine reactions with NOM were modeled for “fast” and “slow” sites, via second order mechanisms (first order with respect to each reactant). A reactive site fraction, defined as the fraction of NOM that reacts with monochloramine, thereby reducing monochloramine and oxidizing NOM, was built into the model.
3. Free chlorine resulting from monochloramine hydrolysis was modeled as reacting with the slow NOM fraction, since hydrolysis of monochloramine is relatively slow. Also, the initial rate results for total free ammonia were not found to influence the reaction order of the empirical rate expression with respect to the fast reactive site fraction.
4. The model was revised to incorporate reactions of free chlorine from monochloramine hydrolysis with the slow reactive site fraction of NOM or with ammonia.

Figure 1 shows an example of the generally good agreement between predicted and observed monochloramine concentrations for four different NOM sources. The monochloramine-NOM reaction model was used as the foundation for the modeling in the studies described below.

Reactions of Monochloramine with Nitrite and Bromide: The oxidation of nitrite and bromide is important because it can result in both chloramine loss and influence DBP formation, depending on the presence of appropriate organic material. The investigators developed a model predicting monochloramine residuals and the role of nitrite in monochloramine loss and incorporated the mechanism proposed by Margerum, et al. (Environmental Science and Technology 1994; 28(2):331-337) into the autodecomposition model. Including this mechanism resulted in good model agreement with experimental results.

The presence of bromide ion in finished drinking water also catalyzes the decomposition of monochloramine. Significant quantities of bromide in finished potable waters could potentially compromise disinfectant residual stability. The reaction model developed for bromide oxidation adequately predicted monochloramine loss and total free ammonia production under chloramination conditions typical for drinking water. The influence of bromide was also tested and modeled in the presence of NOM. As described in the previous section, in the presence of NOM, that initial demand for monochloramine was adequately modeled as a direct reaction between monochloramine and NOM. However, the slow loss of monochloramine was attributed to autodecomposition and monochloramine

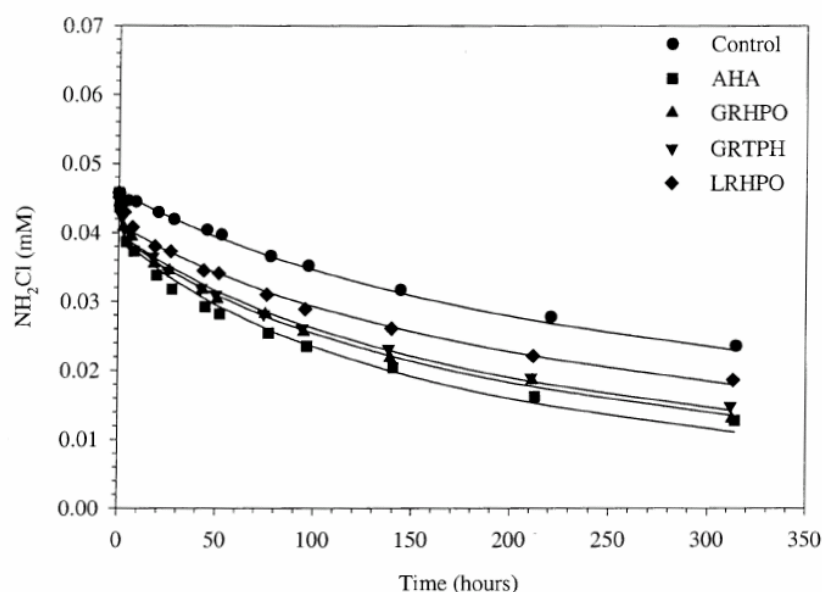


Figure 1. Monochloramine loss in the presence of isolated humic materials at pH 7.6. Lines represent model results, with 95 percent confidence interval. NOM fractions were obtained from the Aldrich Chemical Company (Aldrich Humic Acid, AHA), and two rivers in France (Loire River hydrophobic, LRHPO; Gartempe River hydrophobic, GRHPO; and Gartempe River hydrophilic, GRTPH).

hydrolysis rendering free chlorine available to react with NOM. Counterintuitively, the influence of bromide on the loss of monochloramine does not appear to be additive in the presence of NOM. The researchers attribute this to a reduction in the importance of bromide catalyzed autodecomposition because a large fraction of the active bromine reacts directly to oxidize NOM and does not participate in the autooxidation pathways.

Formation of Haloacetic Acids (HAAs) by Reaction of Monochloramine with NOM: HAA DPB levels in treated drinking water are regulated by EPA due their human health risks. The reaction between monochloramine and NOM results primarily in dihalogenated acetic acids. In the absence of significant bromide concentrations in the raw drinking water, dichloroacetic acid (DCAA) is the dominant HAA formed. The model predicted the formation of DCAA well when compared to experimental results obtained using various sources of NOM over a range of pH and carbonate levels. The model was able to predict the overall formation of DCAA at various monochloramine doses (0.025 and 0.05 mM), but over-predicted DCAA formation at the higher doses (0.1 and 0.2 mM). The researchers suggest that this resulted from an inaccurate representation of the proportion of disinfectant that reacted with NOM in the formation of DCAA.

In the presence of bromide, the formation of dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA) was modeled by apportioning the amount of brominated and chlorinated oxidants that react with NOM. The model was able to adequately predict DBAA and DCAA formation as a function of varying pH and bromide ion concentrations. However, BCAA was initially over-predicted by the model. This suggests that the initial rapid demand for monochloramine in the presence of NOM may not be implicated in BCAA formation, as is observed with DCAA.

Formation of N-nitrosodimethylamine (NDMA): NDMA is a drinking water contaminant of emerging concern at the nanogram-per-liter level, and has been classified as a probable human carcinogen by EPA. It generally is believed that NDMA is formed via the direct reaction of nitrite with an organic nitrogen-containing precursor (such as dimethylamine). NDMA has been found in treated water when it is absent in the influent water, suggesting that it may be formed during treatment through a mechanism other than the classical N-nitrosation pathway. NDMA formation was observed to result from the addition of monochloramine to Iowa River water. In laboratory experiments conducted by the researchers, NDMA formed in the absence of nitrite, which is required for the N-nitrosation pathway. In addition, the capability of the model to predict NDMA formation suggests that key reactions have been accounted for, even though the model includes only a highly simplified representation of NDMA formation. The studies suggest that NDMA can be formed by a direct reaction between monochloramine and dimethylamine. This mechanism involves the intermediate formation of unsymmetrical dimethylhydrazine, which is then oxidized to NDMA, among other products. The researchers concluded that NDMA should be considered a DBP.

Investigator

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For More Information

NCER Project Abstract and Reports:

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/205/report/0

Peer Reviewed Publications

Vikesland, P., Ozekin, K., and Valentine, R.L. 2001. Monochloramine decay in model and distribution system water. *Water Research* 35(7):1766-1776.

Choi, J., and Valentine, R.L. 2002. A kinetic model of N-nitrosodimethylamine (NDMA) formation during water chlorination/chloramination. *Journal of Water Science and Technology* 46(3):65-71.

Choi, J., and Valentine, R.L. 2002. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: A new disinfection by-product. *Water Research* 36(4):817-824.

Choi, J., Duirk, S.E., and Valentine, R.L. 2002. Mechanistic studies of N-nitrosodimethylamine formation in drinking water. *Journal of Environmental Monitoring* 4(2):249-252.

Duirk, S., and Valentine, R.L. 2002. Monochloramine loss in the presence of humic acid. *Journal of Environmental Monitoring* 4(1):85-89.